

measured concentration by theoretical concentration and multiplying by 100. Determine the mean percent recovery for each detector for each QCS triplicate analysis. The RSD for any triplicate analysis shall be  $\leq 10$  percent. For QCS 1 (methylene chloride), the percent recovery shall be  $\geq 90$  percent for carbon as methane, and  $\geq 55$  percent for chlorine as chloride. For QCS 2 (1,3-dichloro-2-propanol), the percent recovery shall be  $\leq 15$  percent for carbon as methane, and  $\leq 6$  percent for chlorine as chloride. If the analytical system does not meet the above-mentioned criteria for both detectors, check the system parameters (temperature, system pressure, purge rate, etc.), correct the problem, and repeat the triplicate analysis of each QCS.

9.1.1 QCS 1, Methylene Chloride. Prepare a stock solution by weighing, to the nearest 0.1 mg, 55  $\mu\text{L}$  of HPLC grade methylene chloride in a tared 5 mL volumetric flask. Record the weight in milligrams, dilute to 5 mL with cleaned PEG, and inject 100  $\mu\text{L}$  of the stock solution into a sample prepared as a water blank (50 mL of cleaned PEG and 60 mL of water in the purging flask). Analyze the QCS according to the procedures described in Sections 10.2 and 10.3, excluding Section 10.2.2. To calculate the theoretical carbon concentration (in mg) in QCS 1, multiply mg of methylene chloride in the stock solution by  $3.777 \times 10^{-3}$ . To calculate the theoretical chlorine concentration (in mg) in QCS 1, multiply mg of methylene chloride in the stock solution by  $1.670 \times 10^{-2}$ .

9.1.2 QCS 2, 1,3-dichloro-2-propanol. Prepare a stock solution by weighing, to the nearest 0.1 mg, 60  $\mu\text{L}$  of high purity grade 1,3-dichloro-2-propanol in a tared 5 mL volumetric flask. Record the weight in milligrams, dilute to 5 mL with cleaned PEG, and inject 100  $\mu\text{L}$  of the stock solution into a sample prepared as a water blank (50 mL of cleaned PEG and 60 mL of water in the purging flask). Analyze the QCS according to the procedures described in Sections 10.2 and 10.3, excluding Section 10.2.2. To calculate the theoretical carbon concentration (in mg) in QCS 2, multiply mg of 1,3-dichloro-2-propanol in the stock solution by  $7.461 \times 10^{-3}$ . To calculate the theoretical chlorine concentration (in mg) in QCS 2, multiply mg of 1,3-dichloro-2-propanol in the stock solution by  $1.099 \times 10^{-2}$ .

9.1.3 Routine QCS Analysis. For each set of compliance samples (in this context, set is per facility, per compliance test), analyze one QCS 1 and one QCS 2 sample. The percent recovery for each sample for each detector shall be  $\pm 13$  percent of the mean recovery established for the most recent set of QCS triplicate analysis (Section 9.4). If the sample does not meet this criteria, check the system components and analyze another QCS 1 and 2 until a single set of QCS meet the  $\pm 13$  percent criteria.

#### 10.0 Calibration and Standardization

10.1 Initial Performance Check of Purging System. Before placing the system in operation, after a shutdown of greater than six months, after any major modifications, and at least once per month during continuous operation, conduct the linearity checks described in Sections 10.1.1 and 10.1.2. Install calibration gas at the three-way calibration gas valve. See Figure 25D-1.

10.1.1 Linearity Check Procedure. Using the calibration standard described in Section 7.2.2.3 and by varying the injection time, it is possible to calibrate at multiple concentration levels. Use Equation 25D-3 to calculate three sets of calibration gas flow rates and run times needed to introduce a total mass of carbon, as methane, ( $m_c$ ) of 1, 5, and 10 mg into the system (low, medium and high FID calibration, respectively). Use Equation 25D-4 to calculate three sets of calibration gas flow rates and run times needed to introduce a total chloride mass ( $m_{cl}$ ) of 1, 5, and 10 mg into the system (low, medium and high ELCD calibration, respectively). With the system operating in standby mode, allow the FID and the ELCD to establish a stable baseline. Set the secondary pressure regulator of the calibration gas cylinder to the same pressure as the purge gas cylinder and set the proper flow rate with the calibration flow controller (see Figure 25D-1). The calibration gas flow rate can be measured with a flowmeter attached to the vent position of the calibration gas valve. Set the four-way bypass valve to standby position so that the calibration gas flows through the coalescing filter only. Inject the calibration gas by turning the calibration gas valve from vent position to inject position. Continue the calibration gas flow for the appropriate period of time before switching the calibration valve to vent position. Continue recording the response of the FID and the ELCD for 5 min after switching off calibration gas flow. Make triplicate injections of all six levels of calibration.

10.1.2 Linearity Criteria. Calculate the average response factor (Equations 25D-5 and 25D-6) and the relative standard deviation (RSD) (Equation 25D-10) at each level of the calibration curve for both detectors. Calculate the overall mean of the three response factor averages for each detector. The FID linearity is acceptable if each response factor is within 5 percent of the overall mean and if the RSD for each set of triplicate injections is less than 5 percent. The ELCD linearity is acceptable if each response factor is within 10 percent of the overall mean and if the RSD for each set of triplicate injections is less than 10 percent. Record the overall mean value of the response factors for the FID and the ELCD. If the calibration for either the FID or the ELCD does not meet the

criteria, correct the detector/system problem and repeat Sections 10.1.1 and 10.1.2.

#### 10.2 Daily Calibrations.

10.2.1 Daily Linearity Check. Follow the procedures outlined in Section 10.1.1 to analyze the medium level calibration for both the FID and the ELCD in duplicate at the start of the day. Calculate the response factors and the RSDs for each detector. For the FID, the calibration is acceptable if the average response factor is within 5 percent of the overall mean response factor (Section 10.1.2) and if the RSD for the duplicate injection is less than 5 percent. For the ELCD, the calibration is acceptable if the average response factor is within 10 percent of the overall mean response factor (Section 10.1.2) and if the RSD for the duplicate injection is less than 10 percent. If the calibration for either the FID or the ELCD does not meet the criteria, correct the detector/system problem and repeat Sections 10.1.1 and 10.1.2.

#### 10.2.2 Calibration Range Check.

10.2.2.1 If the waste concentration for either detector falls below the range of calibration for that detector, use the procedure outlined in Section 10.1.1 to choose two calibration points that bracket the new target concentration. Analyze each of these points in triplicate (as outlined in Section 10.1.1) and use the criteria in Section 10.1.2 to determine the linearity of the detector in this "mini-calibration" range.

10.2.2.2 After the initial linearity check of the mini-calibration curve, it is only necessary to test one of the points in duplicate for the daily calibration check (in addition to the points specified in Section 10.2.1). The average daily mini-calibration point should fit the linearity criteria specified in Section 10.2.1. If the calibration for either the FID or the ELCD does not meet the criteria, correct the detector/system problem and repeat the calibration procedure mentioned in the first paragraph of Section 10.2.2. A mini-calibration curve for waste concentrations above the calibration curve for either detector is optional.

10.3 Analytical Balance. Calibrate against standard weights.

### 11.0 Analysis

#### 11.1 Sample Analysis.

11.1.1 Turn on the constant temperature chamber and allow the temperature to equilibrate at  $75 \pm 2^\circ\text{C}$  ( $167 \pm 3.6^\circ\text{F}$ ). Turn the four-way valve so that the purge gas bypasses the purging flask, the purge gas flowing through the coalescing filter and to the detectors (standby mode). Turn on the purge gas. Allow both the FID and the ELCD to warm up until a stable baseline is achieved on each detector. Pack the filter flask with ice. Replace ice after each run and dispose of the waste water properly. When the temperature of the oven reaches  $75 \pm 2^\circ\text{C}$  ( $167 \pm 3.6^\circ\text{F}$ ), start both integrators and record base-

line. After 1 min, turn the four-way valve so that the purge gas flows through the purging flask, to the coalescing filter and to the sample splitters (purge mode). Continue recording the response of the FID and the ELCD. Monitor the readings of the pressure gauge and the rotameter. If the readings fall below established setpoints, stop the purging, determine the source of the leak, and resolve the problem before resuming. Leaks detected during a sampling period invalidate that sample.

11.1.2 As the purging continues, monitor the output of the detectors to make certain that the analysis is proceeding correctly and that the results are being properly recorded. Every 10 minutes read and record the purge flow rate, the pressure and the chamber temperature. Continue the purging for 30 minutes.

11.1.3 For each detector output, integrate over the entire area of the peak starting at 1 minute and continuing until the end of the run. Subtract the established baseline area from the peak area. Record the corrected area of the peak. See Figure 25D-6 for an example integration.

11.2 Water Blank. A water blank shall be analyzed for each batch of cleaned PEG prepared. Transfer about 60 mL of water into the purging flask. Add 50 mL of the cleaned PEG to the purging flask. Treat the blank as described in Sections 8.2 and 8.3, excluding Section 8.2.2. Calculate the concentration of carbon and chlorine in the blank sample (assume 10 g of waste as the mass). A VO concentration equivalent to  $\leq 10$  percent of the applicable standard may be subtracted from the measured VO concentration of the waste samples. Include all blank results and documentation in the test report.

#### 11.3 Audit Sample Analysis.

11.3.1 When the method is used to analyze samples to demonstrate compliance with a source emission regulation, an audit sample, if available, must be analyzed.

11.3.2 Concurrently analyze the audit sample and the compliance samples in the same manner to evaluate the technique of the analyst and the standards preparation.

11.3.3 The same analyst, analytical reagents, and analytical system must be used for the compliance samples and the audit sample. If this condition is met, duplicate auditing of subsequent compliance analyses for the same enforcement agency within a 30-day period is waived. An audit sample may not be used to validate different sets of compliance samples under the jurisdiction of separate enforcement agencies, unless prior arrangements have been made with both enforcement agencies.

#### 11.4 Audit Sample Results.

11.4.1 Calculate the audit sample concentrations and submit results using the instructions provided with the audit samples.